# THE EFFECT OF DIFFUSION AND FLUID PROPERTIES ON THE YIELD IN CONTACT CATALYSIS

BY

WILMER RAY MANNING

B. Eng., Tulane University, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS

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# THE EFFECT OF DIFFUSION AND FLUID PROPERTIES ON THE YIELD IN CONTACT CATALYSIS

## INTRODUCTION

Marked improvement has been made in recent years in the efficiency of catalytic agents for many gaseous reactions. As a result, the fact that an appreciable part of the total resistance to reaction could be caused by slow transfer of the reactants to the catalyst surface has become increasingly important. A number of theoretical treatments of this subject have been made, but experimental investigations have been few in number and limited in scope. Moreover, most of the investigations have been carried out using packed beds of catalyst; interpretation and generalization of the results have, therefore, been complicated by uncertainties in flow conditions, temperature and concentration distribution, time of contact, and fluid properties.

In the present investigation the relative magnitudes of the diffusional and chemical resistances in a particular gaseous catalytic reaction were studied under conditions such that the flow conditions, temperature and concentration distribution, time of contact, and the fluid properties were accurately known. It was believed that such a study would yield information of fundamental importance in evaluating catalysts and improving equipment for catalytic processes.

The reaction chosen for investigation was the oxidation of sulfur dioxide to sulfur trioxide. Nitrogen, helium, and carbon dioxide were used as carrier gases. The oxidation was carried out in a cylindrical tube of porous material having vanadium oxide catalyst impregnated in the walls. The effects of temperature, time of contact, and nature of the carrier gas on the conversion were studied.

## THEORETICAL

In any heterogeneous catalytic reaction, the rate at which the overall reaction proceeds may be represented as proportional to a driving force divided by a resistance. The driving force is proportional to the difference between the existing average concentration of reactants and the equilibrium concentration. The resistance may be made up of several factors, such as the resistance to dif-

fusion of the reactants to the surface or diffusion of the products away from the surface, resistance to adsorption of reactants or desorption of products at the surface, and resistance to true chemical reaction at the surface. It is generally customary to call the resistance to diffusion of reactants to the surface or diffusion of the products away from the surface the diffusional resistance, dynamical resistance or mass transfer resistance, and to call the resistances to the other three processes mentioned the chemical resistance.

In any particular case, the diffusional resistance is some function of the geometry of the system and of the physical properties of the fluid, while the chemical resistance is a function of the properties of the catalyst and of the particular chemical reaction to be investigated.

Depending on the relative magnitudes of these two resistances, three possible cases may be defined:

(1) If the chemical resistance is very much lower than the diffusional resistance, the overall reaction rate depends entirely on the velocity of transfer of the reacting substances to the catalyst surface. The concentration of the reactants at the surface in this case will be much lower than in the main body of fluid, and can be neglected in comparison with this latter.

(2) If the chemical resistance is very great in comparison with the diffusional resistance the overall reaction rate is determined entirely by the chemical reaction rate at the surface, and the concentration of the reactants at the surface is the same as that in the main fluid stream.

(3) If the two resistances are of the same order of magnitude, both will be important in determining the velocity of the overall reaction.

For the first order heterogeneous catalytic reactions carried out isothermally in cylindrical tubes, with frictionless and non-turbulent flow of the fluid stream, Damköhler *(1)* has shown that the relative magnitudes of the diffusional and chemical resistances in any one of the three cases above can be evaluated by determining the magnitude of the dimensionless group $\frac{k'd}{2D}$. This group represents the ratio of the mean time required for a given quantity of material to diffuse to the wall to the mean time required for the same quantity of material to react at the wall. It is evaluated graphically from a plot of the natural logarithm of the fraction

of reactant unconverted against the dimensionless group $\frac{4DL}{vd^2}$. For values of $\frac{k'd}{2D}$ greater than 100, the diffusional resistance controls the overall rate of reaction, while for values less than 0.1, the chemical resistance largely controls the overall rate. For intermediate values of $\frac{k'd}{2D}$, both resistances will be important in determining the overall rate of reaction.

## EXPERIMENTAL

The apparatus consisted essentially of a catalyst-tube assembly with preheater and exhaust tube; supply tanks for air, helium, carbon dioxide, oxygen, and sulfur dioxide; towers packed with Activated Alumina for drying air and sulfur dioxide; flow meters for each of the gases; a Sargent wet gas meter for calibrating and checking flow meters; suitable pressure regulators for securing constant flow of the various gases; and sampling equipment for analyzing the gases entering and leaving the catalyst tube.

The catalyst tube was a cylindrical tube of Refractory Alundum, ½-inch i.d., ¾-inch o.d., and 23 inches long, having vanadium oxide catalyst impregnated in the walls. Seven Chromel-Alumel thermocouples, equally spaced along the length of the tube, were embedded in the walls to a depth of approximately $\frac{3}{32}$-inch. The electromotive forces generated by these thermocouples were measured by a Leeds and Northrup Portable Precision Pententiometer.

The catalyst tube was enclosed in a cylindrical aluminum casting which was wound with electrical heating coils and was insulated with magnesia lagging. The current to the heating coils was controlled manually by means of variable auto-transformers. With this arrangement it was possible to maintain the temperature of the catalyst tube uniform and constant within plus or minus 2 degrees Centigrade of the desired temperature for as long as desired.

The preheater was a 25-mm. Pyrex glass tube, packed with glass beads. It was wound with electrical coils and insulated with magnesia lagging. The current to the heating coils was controlled manually by means of a variable auto-transformer. A shielded thermocouple was inserted in the preheater and was connected to a Leeds Northrup continuous temperature recorder which indi-

cated the temperature of the gases entering the catalyst tube within $\pm$ 5 degrees Centigrade.

The exhaust tube was provided with a small orifice for mixing the gases prior to sampling, and with a heating coil to prevent condensation of sulfur trioxide.

The gases entering and leaving the catalyst tube were analyzed for sulfur dioxide by a modification of the method of Haller *(2)*. The method involves using sodium hydroxide in the presence of glycerol as an absorbing solution for sulfur dioxide; strongly acidifying and titrating with potassium iodate to the disappearance of the iodine color as indicated by carbon tetrachloride.

Studies were made of the variation in percentage conversion of sulfur dioxide with temperature, time of contact, and nature of the carrier gas.

## RESULTS AND CONCLUSIONS

Data are presented for the isothermal oxidation of sulfur dioxide in the presence of nitrogen, helium, and carbon dioxide as inert gases. The average initial gas composition in each case was 7.8% sulfur dioxide, 19.4% oxygen, and 72.8% inert. The range of variables covered was:

Temperature: 425 to 550°C.
Time of contact: 4 to 15 seconds
Mass velocity: 8 to 67 lbs./hr. $\times$ ft.$^2$
Reynolds' number: 3.5 to 33
Fraction of sulfur dioxide converted: 0.10 to 0.88

The diffusional resistance in the oxidation of sulfur dioxide is less than 10 per cent of the overall reaction rseistance for the specific catalyst and specific conditions investigated. Under other conditions and with other reactions, however, the diffusional resistance may be a much larger fraction of the total reaction resistance, and may largely control the overall rate of reaction. For reactions of the first order in cylindrical tubes, the equations developed by Damköhler *(1)* and used in this work provide a simple method of evaluating the relative influences of diffusional and chemical resistance. The magnitude of the dimensionless group, $\frac{k'd}{2D}$, gives directly the ratio of the diffusional resistance to the chemical resistance. The conditions for diffusional resistance to control the overall rate of reaction in this type of system are: high catalyst activity, large tube diameter, and low diffusivity of reactant.

The specific reaction rate constant for the oxidation of sulfur dioxide is greatly affected by the nature of the inert gas. The rate constant for the reaction in the presence of carbon dioxide is from 1.3 to 2.1 times its value in the presence of nitrogen and from 1.3 to 3.3 times its value in the presence of helium. The reason for this effect of the inert gas is not explained, but it is suggested that it might be caused by differences in the amount of inert gas adsorbed on the catalyst surface, which result in different amounts of surface available for reaction. It is suggested that measurements be made of the relative amounts of helium, nitrogen, and carbon dioxide adsorbed on the type of catalyst used, to aid in deciding whether differences in adsorption will explain the effect of inert gas.

The reaction mechanism is first order with respect to sulfur dioxide and is independent of the concentration of sulfur trioxide over the range of variables covered in the investigation. The investigation was not carried far enough into the equilibrium range to indicate appreciable decrease from the first order reaction rate, but it is apparent that such a decrease must occur as equilibrium is approached.

## NOMENCLATURE

$D$ = diffusivity of sulfur dioxide ($ft.^2/sec.$).

$L$ = length of catalyst tube ($ft.$).

$d$ = diameter of catalyst tube ($ft.$).

$k'$ = specific reaction rate constant for a heterogeneous reaction of first order $\left(\frac{\text{mols converted}/ft.^2 \times \text{sec.}}{\text{mols}/ft.^3}\right)$

$v$ = linear velocity of flow of gas ($ft./sec.$), assumed uniform over cross-section of tube and along the length of tube.

## REFERENCES


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2. Haller, P.: J. Soc. Chem. Ind., 38, 52T (1919).

## VITA

The author was born in McComb, Mississippi, on September 5, 1918. He attended the public schools of that city and upon graduating from McComb High School in 1935 was awarded a four-year Honor Scholarship in Tulane University, at New Orleans, Louisiana. In 1939, having completed his under-graduate work, he received a Bachelor of Engineering degree from that university. In the fall of that year he entered the graduate school of the University of Illinois, where he held successively the positions of Graduate Assistant in Chemistry, Graduate Fellow in Chemical Engineering, Graduate Assistant in Chemical Engineering, and Instructor in Chemical Engineering.